ORDERED ORGANIC SYSTEMS AND MOLECULAR RECTIFIERS

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I. RESEARCH PROGRAM AND PLANS

The major effort of this research program is the fabrication and study of organic and organo-metallic molecular arrays in thin film form. The films are prepared by the Langmuir-Blodgett technique, which permits the deposition of one or two monolayers at a time. Specifically, we have developed the necessary techniques to deposit layers of fatty acids and their salts by this method and are engaged in the determination of their structural and magnetic parameters. The intent of these studies is to enable us to construct two-dimensional arrays whose structures are completely characterized, and to use this knowledge in fabricating two-dimensional magnetic arrays to test various models of magnetic ordering. In addition, an ambitious synthetic organic program is underway with the aim of synthesizing a molecule with asymmetric electron tunneling characteristics. It is planned to create monolayers of such "molecular rectifiers" using the Langmuir-Blodgett technique and to study their electrical characteristics.

II. ACCOMPLISHMENTS

A. MAGNETIC TRANSITIONS IN TWO-DIMENSIONAL STRUCTURES

In the first quarterly report we described the observation of a magnetic transition in a multilayer sample of manganese stearate ($MnSt_2$). Because the $MnSt_2$ is produced by the Langmuir technique the layers contain Mn atoms in planes separated by about 50 Å. This would normally be considered an adequate approximation to a two-dimensional structure. (It is better than any previously reported.) We have improved the sensitivity of our spin resonance technique and have now observed the resonance of single monolayers of $MnSt_2$ on quartz plates. (Some 50 plates were stacked finite distances apart to obtain sufficient signal). This is the first truly lower dimensional magnetic system ever measured.

The characteristics of the monolayer system are different from that of the multilayer. There appears to be a transition to an ordered state, but it occurs at somewhat lower temperatures ($\tilde{\sim}3^{\circ}K$) than in the multilayer ($\tilde{\sim}4^{\circ}K$). The direction of the axis of ordering in the monolayers is parallel to the plane of the quartz, whereas in the multilayers the axis is perpendicular to the substrate. There has been much discussion about "pinning" and other surface effects in magnetism; our observation is a dramatic illustration of such an effect.

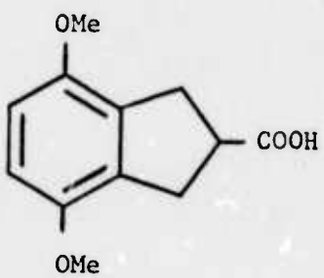
B. STRUCTURE OF $MnSt_2$ FILMS

Our attempts to interpret the x-ray diffraction pattern of multilayer and monolayer films have not been completely successful. A source of the discrepancy that we are currently studying is the roughness of the substrate, or, in general, deviations from planarity of the films. This can be approxi-

imately included in the theory by a Debye-Waller factor of the form $\exp\left(-\frac{16\pi^2}{\lambda^2}\langle z^2\rangle\,\theta^2\right)$, where λ = x-ray wavelength, $\langle z^2\rangle$ is the mean square roughness and θ = glancing angle of the x-rays. Inclusion of this factor improves the overall agreement between calculation and experiment. However it introduces another parameter, $\langle z^2\rangle$, which may make it more difficult to determine unambiguously the structural parameters of the films.

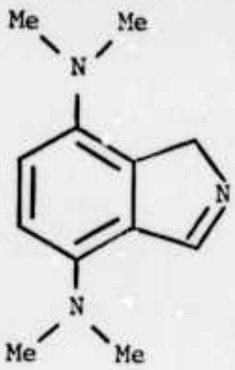
C. MOLECULAR RECTIFIER SYNTHESIS

In the first quarterly report we outlined the detailed synthetic scheme for a molecular rectifier based on a poly-thiophene donor molecule connected to a TCNQ acceptor by means of a rigid bicyclo-octane bridge. This synthesis is shown in the Appendix. Work on reaction sequence 1-9 is presently being carried out to obtain approximately 100 grams of each product; namely,



These reactions involve rather large scale-ups to attain the desired quantities of material, and are approximately half-way to completion.

In addition to this work we have explored the possibility of using a simpler donor system to reduce the large number of steps required to prepare the molecular rectifier. Toward this end we have synthesized the following molecule (III)



We are presently awaiting confirmation of the structure of III, the reduction of which will yield a useful donor.

III. PROBLEMS ENCOUNTERED AND PROGRAM CHANGES

None

IV. FISCAL STATUS

Expenditure and committments to date are on schedule with the contract.

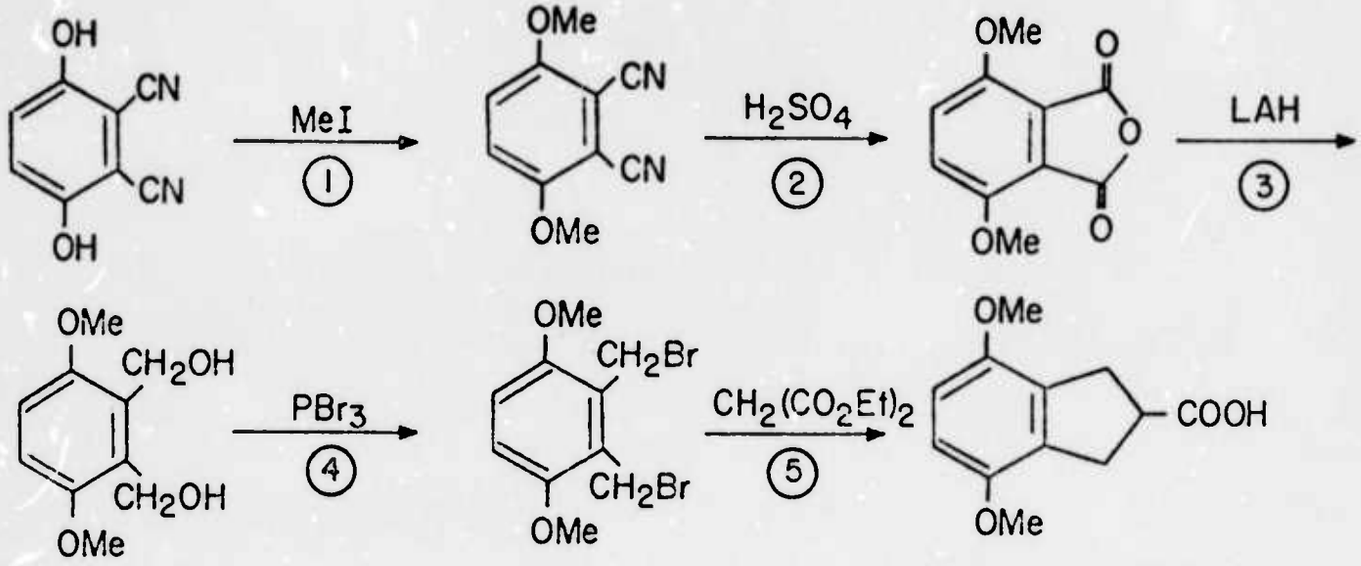
V. FUTURE PLANS

Studies of the effect of the substrate on magnetic transitions will be carried out. We shall attempt to interpose non-magnetic fatty-acid layers between the substrate and the first magnetic layer. Also we will study the dependence of magnetic transitions on the number of magnetic layers. We will also attempt to determine structural parameters of $MnSt_2$ layers, including film roughness. Organic synthesis work is being continued with the expectation of having large quantities of the donor and bridge precursors by the end of the summer.

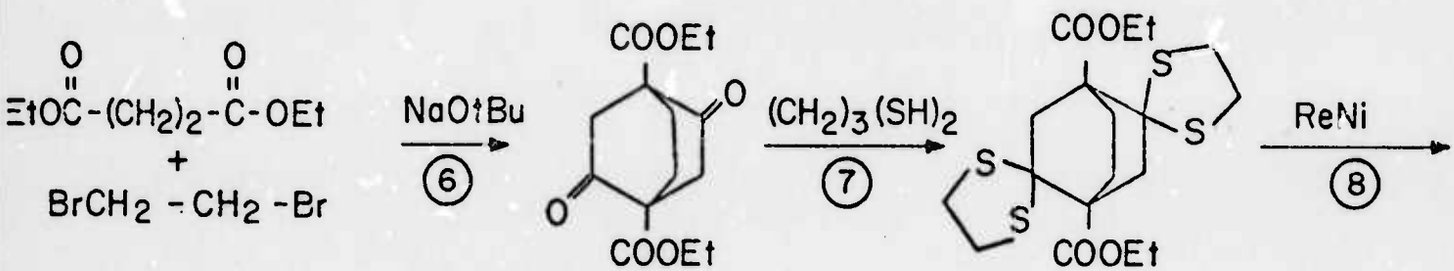
VI. PRESENTATIONS

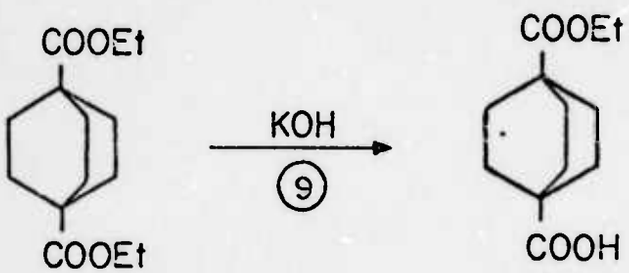
X-Ray Diffraction from Ordered Films of Few Molecular Thicknesses. A.P.S. Meeting, Denver, Colorado, April 3, 1975 (in collaboration with F. Dacol and A. Segmüller).

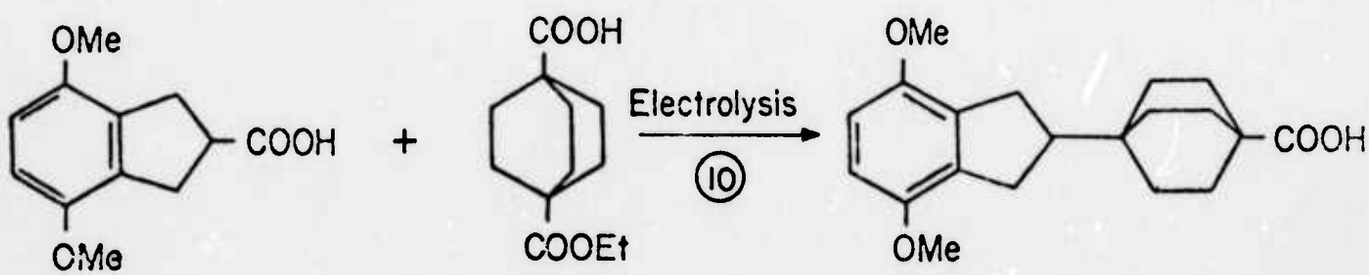
APPENDIX


OH
CN
CN
OH
MeI
①
OMe
CN
CN
OMe
H_2SO_4
②
OMe
O
O
O
OMe
LAH
③

OMe
CH_2OH
CH_2OH
OMe
PBr_3
④
OMe
CH_2Br
CH_2Br
OMe
$CH_2(CO_2Et)_2$
⑤
OMe
COOH
OMe


O
O
EtOC-$(CH_2)_2$-C-OEt
+
$BrCH_2$-CH_2-Br
NaOtBu
⑥
COOEt
O
O
COOEt
$(CH_2)_3(SH)_2$
⑦
COOEt
S
S
S
S
COOEt
ReNi
⑧


COOEt
COOEt
KOH
⑨
COOEt
COOH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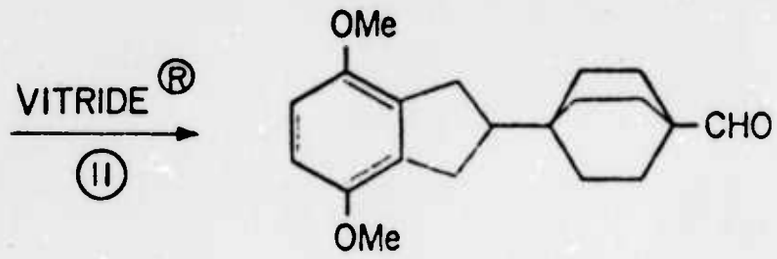
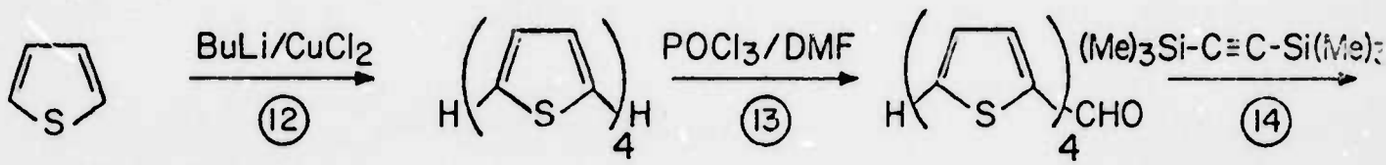
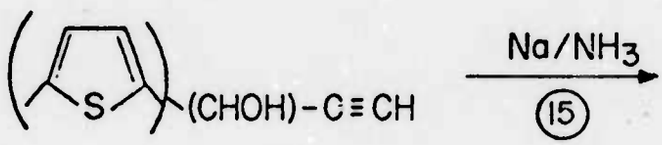
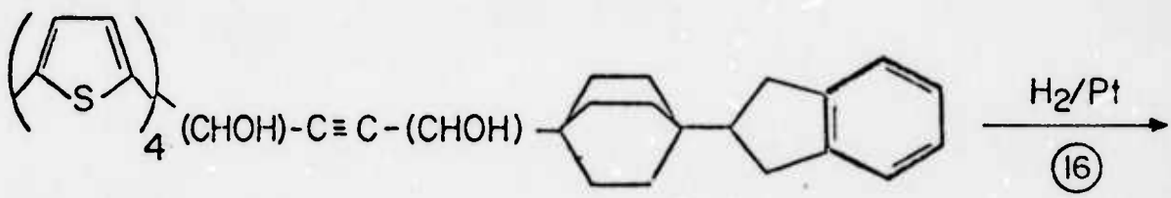
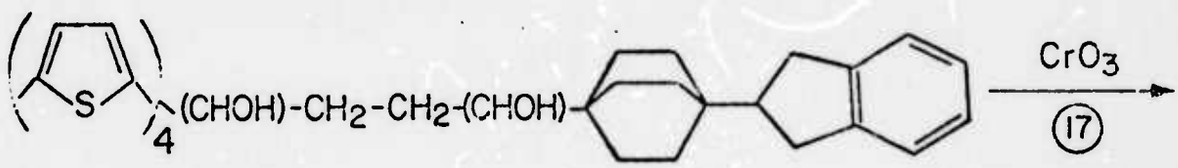
COOH
OMe
+
COOH
COOEt
Electrolysis
⑩
OMe
COOH
OMe

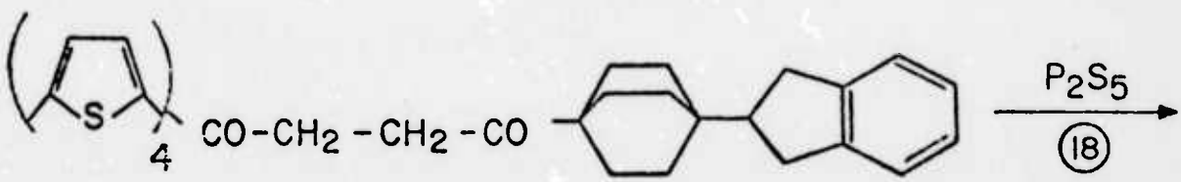

VITRIDE®
(11)
OMe
CHO
OMe

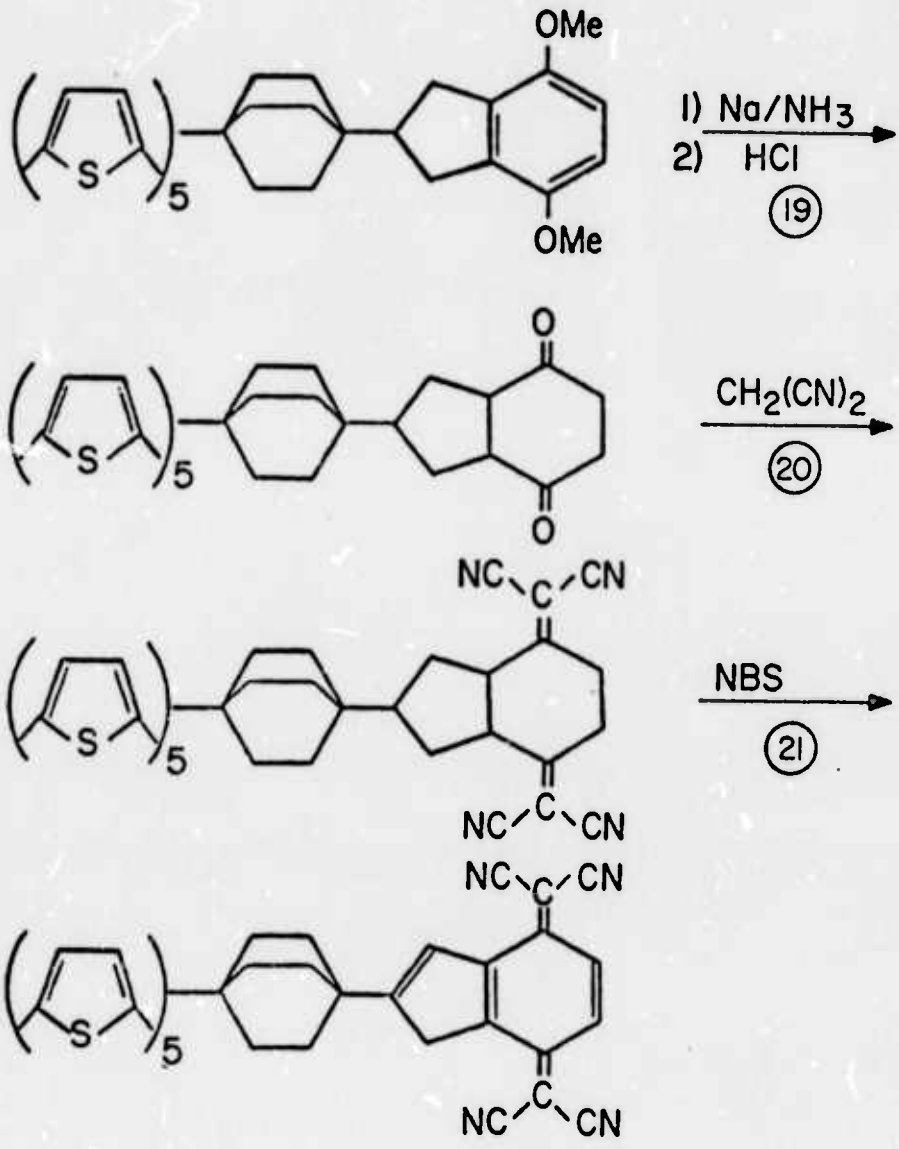

BuLi/CuCl2
(12)
H
S
H
4
POCl3/DMF
(13)
(Me)3Si-C≡C-Si(Me)3
CHO
4
(14)


S
(CHOH)-C≡CH
Na/NH3
(15)


S
4
(CHOH)-C≡C-(CHOH)
H2/Pt
(16)


S
4
(CHOH)-CH2-CH2-(CHOH)
CrO3
(17)


S
4
CO-CH2-CH2-CO
P2S5
(18)


OMe
OMe
S
5
1) Na/NH3
2) HCl
19
O
O
CH2(CN)2
20
NC C CN
NBS
21
NC C CN
NC C CN
NC C CN